

Bulletin of the Agricultural Chemical Society of Japan.

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The Agricultural Chemical Society of Japan.

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The Council of the Agr. Chem. Soc. of Japan has decided to publish English Abstract of those papers appearing in the Journal in a separate form in order to facilitate the circulation in foreign countries.

Bulletin of the Agr. Chem. Soc. of Japan is published for this purpose from May 1926 monthly. The numbering begins with Vol. 2, No. 5. The earlier parts are represented by the English abstracts published in the Journal annexed to the Japanese texts.

The articles to be appeared in the Bulletin must be concise, supplied with experimental methods and data and understandable, without specially referring to the Japanese texts. It ought, however, not exceed four printed pages as a rule. Any longer articles may be accepted according to the decision of the Council, with or without charge for exceeding pages.

Journal of the Agr. Chem. Soc. of Japan will be published in Japanese as formerly. Those desiring the detailed information of the articles appeared in the Bulletin may look for in the Journal of the same Number or the same Volume.

Editor : Umetarō SUZUKI.

Associate Editors : Kakuji GOTŌ and Yoshihiko MATSUYAMA.

ON THE CONSTITUENTS OF THE SHŌCHŪ —JAPANESE WHISKY.

By

MASAKAZU YAMADA

(Received Nov. 10th., 1927)

The ordinary constituents of the 'Shōchū' from miscellaneous raw materials are following :-

	Raw materials etc. (kind)		Alcohol %	Total acid %	Aldehyde %	Furfurol %	Fusel oil %
I	With the new style still (22)	Max.	43.8	0.0048	0.00955	—	0.020
		Min.	31.0	+	0.00209	—	±
		Av.	36.9	0.0009	0.00445	—	0.002
II	Saké cake (23)	Max.	40.6	0.0450	0.02923	0.00240	0.15
		Min.	31.8	0.0060	0.01420	—	0.03
		Av.	37.2	0.0192	0.01919	0.00055	0.07
III	Rice (43)	Max.	42.0	0.0276	0.01570	0.00800	0.15
		Min.	27.0	0.0012	0.00471	—	0.01
		Av.	32.4	0.0094	0.00990	0.00054	0.076
IV	Sweet potato (23)	Max.	39.5	0.0240	0.05571	0.00400	0.50
		Min.	26.6	+	0.00628	—	0.07
		Av.	32.0	0.0090	0.01285	0.00061	0.16
V	Awamori (the special kind) (15)	Max.	43.6	0.0456	0.01021	0.00100	0.28
		Min.	37.5	0.0120	0.00746	0.00032	0.10
		Av.	40.8	0.0247	0.00872	0.00082	0.19
VI	Corean production (13)	Max.	63.4	0.0876	0.03219	0.00400	0.12
		Min.	25.7	0.0024	0.00628	0.00016	0.04
		Av.	37.1	0.0458	0.01144	0.00084	0.07
VII	Wheat etc. (5)	Max.	38.0	0.0120	0.00864	—	0.20
		Min.	36.0	0.0060	0.00667	—	0.06
		Av.	37.0	0.0079	0.00769	—	0.13
VIII	Mixture of I and II (3)	Max.	33.5	0.0162	0.00960	0.00016	0.02
		Min.	32.0	0.0012	0.00585	—	0.003
		Av.	32.8	0.0036	0.00724	0.00005	0.011

Method of analysis:

Total acid: Titrated with $\frac{N}{50}$ NaOH solution.

Furfurol: Determined with aniline acetic acid.

Fusel oil: Estimated colorimetrically, according to T. Takahashi's method modified by R. Sata.

To 1c.c. (or 0.1c.c. is diluted to 1c.c. with water) of sample add 2c.c. of

0.5% vanilline solution in conc. H_2SO_4 and shake. Warm in the boiling water bath for 3 minutes. Add 1c.c. of water and shake. Observe reddish violet color developed after half an hour.

Remarks :

1. There are a few samples in I, which are almost pure ethylalcohol diluted with water. Sometimes deep bluish coloration was observed in the test of the fusel oil. They may be caused by some impurities which have lower boiling points than the ethylalcohol.

2. A large quantity of the aldehyde in II is formed with certainty in the process of heating the extract and consists of acetaldehyde, valeraldehyde, furfurol-like aldehyde etc. (Compare the author's other report.) These aldehydes are the main components of the special flavour.

3. IV is often turbid and generally rich in the fusel oil.

4. VI has frequently a special odor. Richness in acid may perhaps be due to the action of various fungi.

5. Turbidity may be due to the substances which have higher boiling points and lower solubilities in water and accumulate usually in the fraction distills between 90—100°C.

6. VIII, the mixture of I and about its 10% of II in order to forge the flavour of II, would easily be distinguished from II if the aldehyde content were observed.

STUDIES ON THE ACIDS FORMED BY RHIZOPUS SPECIES. PART VI.

THE FORMATION OF MALIC, LACTIC AND FUMARIC ACIDS FROM ACETIC ACID

By

TEIZO TAKAHASHI and TOSHINOBU ASAI.

(Received Nov. 25th., 1927)

In part IV⁽¹⁾ of this report, it has already been pointed out the formation of succinic acid from acetic acid by linking two molecules of the latter and later in part V⁽²⁾ by one of us (T. T.) and K. Sakaguchi, the formation of

(1) Teizo Takahashi and Toshinobu Asai, Bull. of Agric. Chem. Soc. of Japan, Vol. 3, No. 2, 1927.

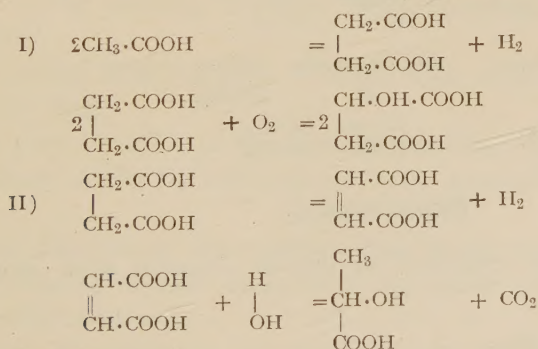
(2) Teizo Takahashi and Kin-ichiro Sakaguchi, Bull. of Agric. Chem. Soc. of Japan, Vol. 3, No. 4—6, p.p. 59—62, 1927.

malic acid from fumaric acid by *Rhizopus* species was also ascertained.

By the further researches upon this point, we were able to confirm the formation of malic, lactic and fumaric acids from acetic acid by this species. The analytical results of the cultures are tabulated below :—

Fungus spec.	Source of N.	Formes of acetates	Duration of culture	Fungus growth (g.)	Acids formed. (g.)				Acetic acid remained (g.)
					Formic acid	Fumaric acid	Malic acid ⁽³⁾	Lactic acid	
Rhiz. G. 34.	Peptone (0.3%)	Na-acet.	45	0.1935	0.0258	0.0985	±	±	1.841
"	"	K-acet.	60	0.2620	0.0225	0.2535	±	±	0.746
"	Am-sulph. 0.312g.	Na-acet.	40	0.1783	0.0220	Trace	±	±	2.643
"	"	Ca-acet.	60	0.1096	0.0068	0.0462	±	±	3.093
"	Peptone 0.3g.(0.3%)	Na-acet.	33	—	+	+	0.1258	±	—
Rhiz. G. 36.	Peptone 0.6g.(0.3%)	Na-acet.	48	0.2015	0.0191	0.1133	±	+	1.625
"	"	K-acet.	70	0.2138	0.0101	0.2140	0.0950	+	0.938
"	Am-sulph. 0.312g.	Na-acet.	42	0.1270	0.0214	Trace	±	+	3.056
"	"	K-acet.	65	0.1570	0.0069	Trace	±	+	1.953
"	"	Ca-acet.	70	0.1396	0.0058	0.0160	±	+	3.034

Accordingly, the mechanism of the formation of these acids from acetic acid may be represented most probably by the following equations :—



As is seen from the table, whatever the species of fungus may be, the amount of fumaric acid formed is always greater in the case of the culture medium which is associated with peptone as nitrogen source than that of one given with ammonium sulphate as such, and this fact is quite reverse when

(3) Malic acid was determined as cinchonin-malate.

referred to the case of the culture to which glucose is supplied as a source of carbon.

The formation of succinic acid from acetic acid in a rather noticeable quantities was observed as stated in previous work¹⁾, in the culture of fungus when acetic acid was supplied as calcium salt. Whereas, by present instance its amount could not be attain more than to just a trace, although the acid was offered in three different formes of salts including *a priori* calcium salt.

There is no adequate explanation as to the real cause of such a phenomenon. Only one condition inducing to this fact being likely due to the difference of the duration of cultivation, inasmuch as the above mentioned equations concerning to the mechanism of the formation of acid are accepted as correct; for special amounts of malic acid formed were being found as stated in the table just in the culture of 33 days, although in other cases nothing but traces of it were met with.

Isolated acids viz. :- malic-, lactic- and fumaric acids are identified by the data given below :-

Free malic acid	Melting point	100°C	(after Pasteur 100°C)
Cinchonin-l-malate	"	197—198°C	(Coinside to Dakin's datum)
Ba-lactate [Ba(C ₃ H ₅ O ₃) ₂]		0.2042g.	
BaSO ₄		0.1501g.	
Ba 0.0884g.		{ Found.	43.51%
		{ Calc.	43.29%
Fumaric acid,	Melting point	284°C	(Uncor. in sealed tube.)
Number of titration :-	Substance taken	0.1g.	
CH·COOH CH·COOH	n/10 NaOH.	{ Found.	17.3c.c.
		{ Calc.	17.2c.c.
Ag-fumarate (Ag ₂ C ₄ H ₂ O ₄)	Substance taken	0.2482g.	
Ag-chloride (AgCl)	"	0.2156g.	
Ag 0.1623g.		{ Found.	65.39%
		{ Calc.	65.43%

Experimental.

The nutrient medium employed in present research were prepared as shown below :-

Distilled water	200c.c.
Peptone	0.6g. (or Ammonium sulphate 0.312g.)
K ₂ HPO ₄ and KH ₂ PO ₄	0.03g. each.
MgSO ₄ and CaCl ₂	0.020g. "
Fl ₂ Cl ₆ , NaCl	each trace.

To the above solution, acetate was added in form of Na-, K-, or Ca-salt for each preparation, corresponding to 2% of free acetic acid viz.; 9.2g.

Na-acetate, 6.4g. K-acetate and 6.0g. of Ca-acetate. Further 0.1% of free acetic acid was added to each solution, prior to the seeding of the fungus, and especially CaCO_3 was added when nitrogen source is given with ammonium sulphate, for the purpose of the neutralization of sulphuric acid, which comes forth naturally step by step in accordance to the growth of fungus proceeds.

After all, we were able to obtain as the concentrations of hydrogen ions of the culture media in their initial state as shown below :—

Forms of acetates	Forms of nitrogen source	P _H
Na-acetate	Peptone	5.7
"	Am-sulphate	5.8
K-acetate	Peptone	5.8
"	Am-sulphate	5.8
Ca-acetate	Peptone	6.0
"	Am-sulphate	5.6

The temperature of the culture through whole period was 25—30°C.

The detection and identification of fermentation products.

Aldehyde :

The filtrate from the fungus growth behaving as alkaline reaction to litmus, the distillate⁴⁾ under reduced pressure was neutralized by sulphuric acid and redistilled so as to free aldehyde as much from water as possible and concentrate it. In first part of this redistillate aldehyde was detected by the three reactions viz. :— a, by decolorised fuchsin solution. b, by Nessler's reagent. c, by reducing faculty of Fehling's solution in hot state.

Ethyl alcohol.

The neutral distillate gave iodoform when treated by common way.

Volatile acids :

The neutral residue of the distillate mentioned above, was acidified more or less strong acidity by sulphuric acid with association of tropæolin OO as an indicator.

In the distillate of this acidified fluid formic acid was detected by the reducing property of both ammoniacal Ag-nitrate solution and aqueous mercuric chloride solution.

Further, formaldehyde was given from the dry distillation of calcium salt of this acid.

To determine formic acid quantitatively the distillate was neutralised with NaOH solution, and then added aqueous mercuric chloride solution associated with Na-acetate prior to heating, thus converting soluble mercuric salt into

4) It gave yellow ppts. by Nessler's reagent.

insoluble ones, which may be determined gravimetrically. (Portes-Ruyssen's method)

Acetic acid was determined by titrating the distillate which was previously freed from formic acid by treating the mixture of both acids with a mixture of potassium bichromate and sulphuric acid.

Non-volatile acids :

These acids were gained as a mixture in the ether extracts of the residue from volatile acids. After concentrating the extracts by evaporation, there comes forth *inter alia* the characteristic crystals of fumaric acid, which gave positive colour reactions to both resorcin⁵⁾ and β -naphthol⁶⁾ in presence of sulphuric acid.

The filtrate from the crystals of fumaric acid gave colour reactions for lactic-, succinic- and malic acids⁷⁾.

Lactic acid was separated from other acids as barium salt, which being soluble in 80% of alcohol.

To identify malic acid from the mixture of both malic and succinic acids, it was isolated as cinchonin-l-malate after Dakin's method.

A NEW COLORIMETRIC METHOD FOR THE DETERMINATION OF SULPHUROUS ACID IN THE FOOD PRODUCTS

By

RINJIRO SASAKI.

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(Received Dec. 5th., 1927)

Principle of the Method

The principle of the method consists in the distillation of sulphurous acid from the material in a current of carbonic acid, and subsequent development of a brilliant blue color produced by the reduction of the molybdenum. The reduction is accomplished by the sulphurous acid present in the distillate in the faint alkaline medium of dilute ammonium hydroxide.

Preparation of the Reagents

(A) Phosphomolybdic acid solution: This is prepared by dissolving

5), 6), 7) Jour. of Agric. Chem. Soc. of Japan, Vol. I, No. 14.

8) Dakin, Journ. of Biol. Chem., Vol. LXI, No. 1, p. 139, 1924.

5 gms. of pure crystal of phosphomolybdic acid (E. Merck) in water to 100 ccm.

(B) Ammonium hydroxide solution: This is prepared by diluting 10 ccm. of conc. ammonium hydroxide to 200 ccm. with water, and the solution of sp. gr. 0.994 is most suitably used.

Method of Determination

Distillation of sulphurous acid:— Place 10—50 gms. of the material in a 500 ccm. flask (glass-stoppered), add water, if necessary, and 5 ccm. of a 20% solution of phosphoric acid, and distil in a current of carbonic acid into water containing 10 ccm. of NH_4OH (sp. gr. 0.994), until 60—80 ccm. (for about 60 minutes) have passed over. To avoid escape of sulphurous acid, the condenser tube should dip below the surface of the NH_4OH solution.

The method and apparatus may be simplified without material loss in accuracy by omitting the current of CO_2 , adding 10 ccm. of phosphoric acid instead of 5 ccm. and pouring into the distilling-flask 10 ccm. of saturated NaHCO_3 solution, immediately before attaching the condenser.

Developement of color:— When the distillation is finished, 5—10 ccm. of ammonium hydroxide solution are added, followed by 5—10 ccm. of phosphomolybdic acid reagent and the contents are mixed, and transferred to a 100 ccm. glass-stoppered volumetric flask. Water is added to 100 ccm., and the contents are thoroughly mixed, and allowed to stand 20 minutes. The color is read in the colorimeter against the standard.

Preparation of Standard

1 ccm. of a solution of $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ containing 0.05 gms. of SO_2 per 100 ccm. (1.9682 gms. of $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ (E. Merck) in 1000 ccm.) is measured into a 100 ccm. glass-stoppered volumetric flask. 5 ccm. of NH_4OH are added, followed by 5 ccm. of the phosphomolybdic acid reagent.

The treatments are carried out at the same time and in the same manner with both the standard and the distillate of the unknown.

Calculation

When the unknown is made up to 100 ccm. and the standard solution is set at 20 in the colorimeter, the calculation is as follows.

$$\frac{20}{\text{unknown}} \times 0.5 = \text{mgr. of } \text{SO}_2 \text{ in the sample.}$$

If the amount of SO_2 in the unknown is less than 1 mgr., the better result is obtained by using the Nessler's colorimetric tubes.

Miscellaneous Complements

The developement of a brilliant blue color produced by the reduction of the molybdenum is in direct proportion to the amount of sulphurous acid (or sulphite) present. It is able to determine quantitatively the developement of color by colorimeter as long as the amount of sulphurous acid in the sample does not exceed double the quantity, or is not less than half the quantity present in the standard. So that the standard should be prepared as that the color produced by the reduction to be near to that of the sample.

A solution of phosphomolybdic acid was prepared so that 2 ccm. was reduced by approximately 5 mgr. of SO_2 (10 ccm. of the standard solution). Uses of the reagents in excess are desired, but the amounts of two reagents should be used always in the same volume, so that the yellow color of the excess of phosphomolybdic acid disappear by the action of ammonium hydroxide.

The sulphurous acid that combined with aldehydes or ketones such as formaldehyde, acetaldehyde or acetone can not be determined.

Sugars, alcohols, organic acids and salts do not interrupt the above method of determination.

As phenols and phenol-carboxylic acids (such as gallic acid) reduce the phosphomolybdic acid in the same manner as sulphurous acid, so the above colorimetric method can not be applied directly in the material which contains tannin or phenolcompounds. (Author's abstract.)

THE POTENTIOMETRIC TITRATION OF CHLORINE IN SOILS

By

K. KAWAMURA and B. SAITO.

(Received Dec. 15th., 1927)

The potentiometric titration was employed for the determination of chlorine in 14 soils of different origin, the silver electrode being used. The amount was found to be from 0.006 to 0.03%. The volcanic ashes fallen in October, 1927 from Asama Volcano, contained 0.055% Cl.

The potentiometric titration furnishes an accurate method for the determination with colored extracts of soils.

ON THE EXCHANGEABLE BASES IN SOILS.

By

MITSURU HARADA.

(Received Dec. 12th., 1927)

This investigation deals with the estimate of exchangeable bases and the degree of saturation of mineral soils. Subsequent experiments were made on the fraction of soils below 0.5 mm. in diameter.

1. The exchangeable bases were determined by Hissink's method. The average values of the exchangeable bases of 7 soils whose P_H values are greater than 5.5 and those of 7 soils whose P_H values are smaller than 5.5, are given in the following table. The P_H values were estimated by Biilmann's quinhydrone electrode in the water soil suspension with the soil-water ratio of 1 : 5.

P_H	Mgm equivalents of exch. bases per 100 g. of dry soils.				Percentages of exch. bases in total bases.			
	Ca	Mg	K	Na	Ca	Mg	K	Na
5.50—6.43	15.7	3.5	1.0	2.4	69.5	15.5	4.4	10.6
4.48—5.44	2.5	2.8	1.1	2.7	27.5	30.8	12.1	29.6

The above table shows that acid soils are markedly deficient in exchangeable calcium.

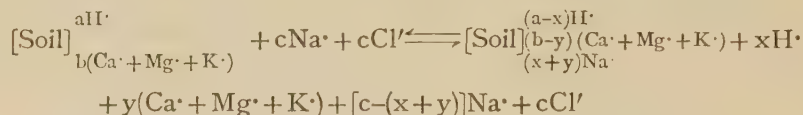
2. The absorption capacity was estimated by Bobko's method. The absorption capacity (in mg. equivalents of the Ba absorbed by soils) correspond to the sum of the total exchangeable bases and the H-ions replaced by Ba-ions. Hence the difference between the absorption capacity and the H-ions represents the total exchangeable bases. The results thus obtained and the total exchangeable bases by Hissink's method are as follows:—

Soil No.	Mg. equivalents per 100 g. of dry soils.			
	Bobko's method.			Total exch. bases (Hissink's method)
	Absorption capacity.	H-ions.	Difference	
1	13.80	0.18	13.62	13.79
2	14.79	0.17	14.62	14.74
3	14.49	1.25	13.24	13.87
4	25.90	0.08	25.82	25.99
5	17.48	0.18	17.30	17.33
6	10.98	3.30	7.68	7.16
7	39.13	0.73	38.76	38.13
8	7.84	0.35	7.49	10.48

9	2.22	0.04	2.18	6.09
10	13.08	8.00	5.08	5.85
11	78.40	62.64	15.76	15.08
12	21.50	2.82	18.68	18.95
13	12.85	8.30	4.55	3.95
14	15.95	4.83	11.15	10.24
15	35.54	1.38	34.16	34.14
16	3.58	0.92	2.66	3.30

From the above table it will be seen that both the results agree well except No. 8 and 9 which are infertile volcanogeneous soils.

3. A new method for estimating the degree of saturation was studied. According to Page, when the soils are treated with the solution of NaCl, the following equilibrium of ionic exchange takes place:—



And he pointed out that if, however, the soil contains CaCO_3 , the above equilibrium will be disturbed by the reaction between the displaced H-ions and the CaCO_3 , thus:



If the mixture of soils and CaCO_3 were leached with sufficient amount of NaCl solution, this process could go on until the whole of the exchangeable H-ions had been replaced by Na^+ ions.

By this principle, the degree of saturation may be estimated. The procedure is as follows: the mixture of 25 g. of soils and 1 g. of CaCO_3 is shaken in a beaker with 100 c.c. of normal NaCl solution, heated to 90° for an hour, and allowed to stand over night. The mixture then is washed with the same solution until two successive liters of extracts are obtained. The calcium in the extracts are determined in the usual way. The difference in the Ca contents of the first and the second-liter portions (L) represents the sum of the Ca-ions directly replaced from the soils (L') and the quantity of Ca equivalent to the exchangeable H-ions (h). The total bases (T) which soils are capable of binding are equal to the sum of the exchangeable bases actually present in soils (S) and the exchangeable H-ions (h). Consequently, the degree of saturation (V) is given by the formula:

$$V = \frac{s}{h+s} \times 100 = \frac{S}{T} \times 100, \text{ where } h = L - L'$$

The values of S and L' are determined by Hissink's method.

The results thus obtained, the degree of saturation by Hissink's method, hydrolitic acidity estimated by Kappen's method, and P_H values are given in the following table :-

Soil No.	Mg. equivalents per 100 g. of dry soils-		$\frac{s}{h+s}$	V (Hissink's method)	Hydrolitic acidity	P_H
	h	s				
1	12.57	13.79	52.3	25.3	15.55	6.08
2	11.91	14.74	55.2	28.6	14.00	6.03
3	14.75	13.87	48.5	25.1	22.41	5.78
4	8.82	25.99	74.7	37.0	13.05	6.43
5	13.89	17.33	55.5	28.6	17.43	6.06
6	15.64	7.16	31.4	17.4	21.28	5.44
7	11.29	38.13	77.2	37.6	13.95	6.00
8	20.75	10.48	33.6	17.1	14.32	5.45
9	38.52	6.09	13.6	2.4	10.15	5.94
10	32.66	5.85	15.2	9.8	42.51	4.80
11	79.21	15.07	16.0	9.8	251.33	4.48
12	10.21	18.95	38.5	20.0	33.73	5.21
13	17.82	3.95	18.1	12.2	33.42	5.26
14	15.29	10.24	40.1	22.1	23.65	5.19
15	14.04	34.14	70.9	34.3	22.06	6.00
16	14.61	3.30	18.4	8.1	16.30	5.30

From the above table we find that :-

(1) The degree of saturation of this method is about twice that of Hissink's method.

(2) There is a connection between the exchangeable H-ions (h-values) and hydrolitic acidity. With high h-values we generally find high hydrolitic acidity.

(3) The degree of saturation of this method can be correlated with the P_H values.

4. The degree of saturation of Gehring's method was compared with that of this method. The degree of saturation of Gehring's method is the ratio of the exchangeable calcium in soils (L') to the total calcium (L) which the soils could hold, when the exchangeable H-ions were replaced Ca-ions in $\text{Ca}(\text{OH})_2$ solution. The values of $\frac{L'}{L} \times 100$ of Gehring's method are smaller than that of this method. If, however, in Gehring's method CaCO_3 be added after the soils have been treated with saturated $\text{Ca}(\text{OH})_2$ solution, the results agree well with that of this method.

The data obtained are as follows :-

Soil No.	$\frac{L'}{L} \times 100$		
	Gehring's $\text{Ca}(\text{OH})_2$ method	$\text{Ca}(\text{OH})_2 + \text{CaCO}_3$ method	The author's CaCO_3 method.
1	35.9	40.1	41.0

2	38.2	43.1	43.2
3	32.4	36.7	36.4
4	56.3	67.6	68.3
5	39.8	47.4	46.8
6	13.0	15.2	14.6
9	0.9	1.0	1.0
12	23.7	28.8	28.8
16	3.0	3.7	3.7

RESEARCH ON ELECTROLYTIC REDUCTION POTENTIALS. (PART IV.)

ON THE REDUCTION POTENTIALS OF KETONIC RADICALS AND THEIR RELATIONS TO THE CONSTITUTIONS.

By

MASUZO SHIKATA and ISAMU TACHI.

(Received Dec. 12th., 1927)

Summary:

(1) The electrolytic reduction potentials of ketonic compounds such as diacetyl, acetoin, acetone, methylethylketone, acetophenone, benzophenone, benzil, benzoin were measured with the dropping mercury cathode and the polarograph.

(2) In order to show the relation of reduction potentials of these compounds to their concentrations and hydrogen ion concentrations, the so-called theoretical values were calculated by the Nernst formula of the reversible reduction type, and were compared with the observed values at 25°C.

$$\pi = -\frac{0.05911}{2} \log \frac{k'}{[H^+]^2 [\text{reducible compounds}]}$$

(3) For diacetyl, if the R. P. (-0.345 V) (from 1n calomel electrode) of the $1.13 \cdot 10^{-3}$ mol in (0.01n HCl + 0.1n KCl) solution was taken as a standard, we found

$$\log k' = 4.681$$

The observed reduction potentials showed relatively small deviations from the calculated values in the acidic solutions, but in the alkaline solutions the observed R. P. were more positive than the calculated R. P.

(4) In the case of acetone, $\log k' = 34.941$, and the R. P. (obs.) showed much larger negative deviations and could not be regarded as reversible.

For methylethylketone $\log k' = 34.418$, that is to say, methylethylketone is more easily reducible than acetone, although their difference is not conspicuous.

(5) For acetoin, $\log k' = 30.453$, and the deviation from the calculated values were about the same magnitudes as in the case of acetone.

(6) For acetophenone $\log k' = 28.235$.

(7) In the cases of benzophenone, benzil and benzoin, a certain amount of ethyl alcohol was added to the electrolysing solution, and as the ethyl-alcohol was found to make the reduction potential negative, we did not calculate $\log k'$.

We may say from the results of the experiments that the reduction potentials of aromatic ketones showed much smaller deviations than those of aliphatic ketones and that the reductions of the aromatic ketones have a reversible character, although the present authors have the view that there seems to be no definite difference or discontinuity between reversible and irreversible reductions. In the alkaline solutions the R. P. of aromatic ketones showed larger deviations than in the acidic, and moreover, the direction of the deviations were reversed, that is, the R. P. (obs.) in alkaline solutions were much positive than the R. P. (calc.)

Further, the polarograms of aromatic ketones showed typical saturation curves, while those of the aliphatic ketones were slowly increasing and did not show definite saturation curves. So we may say, that a minute quantity of an aromatic ketone in a solution may more easily be determinable by the polarographic method than an aliphatic ketone.

(8) The solubility at 25°C of the following compounds in water were determined by the polarographic method.

Benzophenone	$4.41 \cdot 10^{-4}$ g. mol. per liter.
Benzil	$8.86 \cdot 10^{-5}$ " " "
Benzoin	$1.51 \cdot 10^{-4}$ " " "

(9) The group effects of CH_3 , C_6H_5 , CO , OH on the reducibility of ketone radical are noteworthy.

If we compare the reduction potentials of the solutions, containing about 10^{-4} mol. of reducible substances in (0.01N HCl + 0.1N KCl) mixture, we reach the following.

	Diacetyl CH_3 CO CO CH_3	Acetoin CH_3 CO CH(OH) CH_3	Acetone CH_3 CO CH_3	Aceto- phenone CH_3 CO C_6H_5	Benzophenone C_6H_5 CO C_6H_5	Benzoin C_6H_5 CO CH(OH) C_6H_5	Benzil C_6H_5 CO CO C_6H_5
Concentration ($\times 10^{-4}$ m.)	1.13	1.13	1.03	1.054	1.0	1.0	1.0

R. P.	-0.402	-1.139	-1.278	-1.116	-1.013(II)	-0.953(II)	-0.203
Diacetyl	0	-0.737	-0.876	-0.714	-0.326	-0.551	+0.199
Acetoin		0	-0.139	+0.023	+0.126	+0.186	+0.936
Acetone			0	+0.162	+0.265	+0.322	+1.075
Acetophenone				0	+0.103	+0.163	+0.913
Benzophenone					0	+0.060	+0.810
Benzoin						0	+0.750
Benzil							0

As is seen in the above table, the differences of the compounds $R \cdot CO \cdot R$ and $R \cdot CO \cdot CO \cdot R$ are

Acetone and Diacetyl	-0.876 V
Benzophenone and Benzil	-0.810 V

Those of $R \cdot CO \cdot R$ and $R \cdot CO \cdot CH(OH) \cdot R$ are

Acetone and Acetoin	-0.139 V
Benzophenone and Benzoin	-0.060 V

The C_6H_5 group makes CO more easily reducible than CH_3 group as the following

Acetone and Acetophenone	-0.162 V
Acetophenone and Benzophenone	-0.103 V

The substitution of two CH_3 and C_6H_5 makes reduction potential about 0.2 Volts.

Diacetyl and Benzil	-0.199 V
Acetoin and Benzoin	-0.186 V
Acetone and Benzophenone	-0.265 V

We see from the above comparisons that there seems to be a definite group effect and an effect of orientation of a group on a reduction potential of a ketonic group, not only in a qualitative, but also in a quantitative sense, although not in a satisfactory degree.

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ON THE DETERMINATION OF DEGUMMING POWER OF SOAPS (BOILING-OFF SOAPS).

By

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Introductory.

According to a preliminary report by the author, the scouring power of

soap on raw silk has a relation with the degree of hydrolysis of that water solution; that is, the greater the hydrolysis of soap solution, the greater the degumming power.

However, we can mention several different methods of determining the degree of hydrolysis of soap solution, such as: Titration method, Toluene method, Salting-out method and the method of Electro-conductivity. Among these methods, I can find many differences such as: the difficulties of operation, the accuracy of the determined results, etc., but according to my investigations, I can mention which is the best method of all. That is the Titration method. However, the soap which is used for silk scouring usually undergoes some changes in its property while in storage; the soap will suffer some chemical change in the air-oxidation and the hydrolysis of that soap is changed. Consequently, it acts differently in the scouring of raw silk.

Experiments.

PART I.

The methods of determining the hydrolysis of soap can be classified as follows:

- (a) Dropping common salt into a water solution of soap; the soap is salted-out and next the mother liquid is filtered off, dissolving the salted-out soap in alcohol and then the free fatty acid is titrated by alkali. This is the salting-out method.
- (b) The alkali which is developed by the hydrolysis of soap can be titrated with diluted acid using phenolphthalein as indicator.—Titration method.
- (c) Adding toluene into the hydrolysed soap solution and dissolving the fatty acid which comes from the hydrolysis of soap. Evaporated toluene and weigh the residual fatty acid.—Toluene method.
- (d) Determining the electro-conductivity of the soap solution by the Wheatstone-Bridge Electro-conductivity method.

Experimental results.

I. Salting-out Method. The hydrolysis degrees of sodium soap of stearic, palmitic and oleic acids by the salting-out method are too small compared with those of other methods and the hydrolysis degrees are not corresponding to their scouring powers.

II. Titration Method. By this method I determined the hydrolysis degree of a soap solution by means of titration with diluted oxalic acid (acidity is known), dropping it into the hydrolysed solution using phenolphthalein. However, in this method we can only determine the end-point of the hydrolysis and not the hydrolysis itself before the neutralization by acid begins.

The experimental results were as follows :

TABLE I.

Names of Soaps.	Hydrolysis degrees	Loss on scouring (scouring power)
Na-soap of stearic acid	55.16%	11.43%
Na-soap of palmitic acid	46.14	10.86
Na-soap of oleic acid	44.98	10.29

This is the average value of eight experiments and the boiling-off operation is carried out in 0.1% solution of soap. I used a much more diluted solution of soap than usual in order to make the differences between three kinds of soaps clearer.

Another experiment is carried out in a different concentration of soap and the result is tabulated as follows :

TABLE II.

Names of Soaps.	Hydrolysis degree.	Loss on scouring (scouring power)
Na-soap of olive oil (a)	52.41%	10.38%
Na-soap of olive oil (b)	59.63	15.91

In this experiment shown in table II, the concentration of the soap solution is 0.5%, and the boiling-off operation is carried out in shorter time than usual in order to make the differences of scouring powers clearer.

Another experiment which is carried out with eight different kinds of soaps prepared from different kinds of oils shows the following results :

TABLE III.

Names of Soaps.	Hydrolysis degree by Tit. method :	Loss on scouring. %	
		20m boiling-off.	40m. b.-o.
Na-soap of Yamacha oil	37.5%	16.83	18.44
" Olive "	36.5	16.78	18.36
" Castor "	13.0	9.14	11.01
" Soya Bean "	changed so much that Titration method cannot be applied.	2.25	3.28
" Cotton Seed "		2.03	2.04
" Peanut oil "		7.65	10.96
" Tallow "	52.0	17.73	18.42
" Coconut Oil "	22.5	12.23	13.70

According to these experimental results, I concluded that the greater the hydrolysis degree of the soap solution, the greater is the degumming (scouring) power of that soap.

III. Toluene Method. By the Toluene method we can determine the hydrolysis degree of soap solutions as follows ;

Dropping toluene into the water solution of soap (enough to dissolve fatty acids developed by the hydrolysis of soap), the fatty acids will be removed to the layer of toluene; then we separate the solution from that of the toluene by means of a separating funnel. After these operations, the toluene will be distilled off and the residual fatty acids can be weighed. The ratio of these fatty acids to the total contained in the soap will denote the hydrolysis degree of the soap solution. Comparing the experimental results with those of the Titration-method, I have the Table IV.

TABLE IV.

Names of Soaps.	Hydrolysis degree by Toluene-method.	Loss on scouring.	Hydrolysis deg. by Titration-m.
Na-Soap of Stearic acid	53.29%	18.35%	59.59%
" Palmitic "	41.59	18.14	49.62
" Oleic "	38.31	17.94	42.43

Just as in the case of the Titration-method, the hydrolysis degree which is determined by the Toluene-method can denote the scouring power of the soap solution. There are some differences among the degree of hydrolysis determined by the above two different ways with the same solution of soap, but the order is the same.

IV. Electro-Conductivity Method. In this method we use the Wheatstone-Bridge and determine the conductivity of the soap solution. If it be determined we can calculate the hydrolysis degree by the following formulae:

$$X = \frac{\lambda_v - \lambda_{v'}}{\lambda_{v''} - \lambda_{v'}} \quad \text{where } X = \text{hydrolysis degree.}$$

λ_v = equivalent conductivity of soap solution.

$\lambda_{v'}$ = " " " " " " when it is dissolved in alkali solution.

$\lambda_{v''}$ = equivalent conductivity of alkali solution.

By this method one can determine the true hydrolysis of a soap solution, yet the operation is very complicated and is not practicable in factories.

From these experiments I conclude that the scouring power of any soap can be judged before using it in the scouring operation by simply determining its hydrolysis degree of its water solution by Titration-method.

PART II.

The reason why the Toluene-method cannot be applied to the soaps which undergo oxidation.

As can be seen from Table IV the degree of hydrolysis determined by

the Toluene-method is somewhat smaller than that of the results determined by the Titration-method. While I have been investigating the hydrolysis of several commercial soaps, by these two different methods I have obtained very instructive results, that is, when the soap has undergone a change in the chemical composition or, in other words, when the fatty acids are oxidised in the air, the hydrolysis degree of such soap is greater by the Toluene-method than by the Titration-method. The reverse is true for fresh soap solutions.

I examined the hydrolysis degree of the twelve commercial soaps (one of which is made in France and the others are home-made) by the two methods above-mentioned. The results are as follows: (Where the soap solution is in $\frac{N}{50}$ solution and the oxalic acid concentration is $\frac{N}{10}$, the quantity of toluene is 50 c.c. to each 200 c.c. of soap solution.)

TABLE V.

Names of Soaps,	Degree of oxidation	Hydrolysis degree (%)		Difference.
		by Tit. m.	by Tol. m.	
L.	little	37.00	21.50	--12.50
J.	very little	31.50	19.75	-11.75
K.	" "	33.25	22.75	-10.50
A.	much	33.50	23.50	-10.00
C.	little	34.75	27.25	- 7.50
D.	"	31.25	24.00	- 7.25
B.	much	30.25	23.25	- 7.00
G.	"	26.25	23.75	- 2.50
E.	little	25.25	23.25	- 2.00
F.	very much	23.25	25.00	* + 1.75
H.	" "	17.50	24.75	* + 7.25
I.	" "	16.25	28.75	* +12.50

In this Table the oxidation degree is determined by the quantity of so-called ASE or Sweat of the soap and the author has found that the degree of oxidation of fatty acid which composes soap is in proportion to the quantity of the sweat of that soap. On this problem, the author will publish another essay, the title of which will be "ON THE SO-CALLED ASE or SWEAT OF SOAPS".

We have already seen in Table IV that the hydrolysis degree determined by the Toluene-method is smaller than that of the Titration-method in the case of a single fatty acid soap such as stearic, palmitic and oleic acid. According to Table V, the same relations also hold excepting three cases which are arranged at the end of this series. These three soaps which are ex-

ceptional, produce a greater quantity of sweat and the fatty acids in them are largely oxidised; in other words, the hydrolysis degree determined by the Toluene-method of the soaps which have suffered oxidation is larger than that of the Titration-method. This phenomena has a very interesting relation considering the scouring power of these soaps. The results of the investigating the scouring power of these soaps are as follows:

TABLE VI.

Names of Soaps	Hydrolysis degree.		Scouring power. (Loss on scouring).
	Titration-m.	Toluene-m.	
L.	37.00%	24.50%	15.94%
J.	31.50	19.75	15.85
K.	33.25	22.75	15.89
A.	33.50	23.50	14.85
C.	34.75	27.25	15.46
D.	31.25	24.00	14.09
B.	30.25	23.25	15.26
G.	26.25	23.75	13.12
E.	25.25	23.25	13.16
F.	23.25	* 25.00	* 11.61
H.	17.50	* 24.75	* 11.89
I.	16.25	* 28.75	* 11.71

According to Table VI it can be seen that the soaps which denote greater hydrolysis by the Toluene-method than by the Titration-method, that is, the soaps F, H and I in the Table VI, have a smaller percentage of scouring power on raw silk instead of greatness of their hydrolysis degree by the Toluene-method. In other words, the hydrolysis degree by the Toluene-method in these cases does not denote their scouring powers. To find the reason of this, I have taken two different kinds of soaps as samples, the one a sodium soap of tallow and the other that of soya bean oil. These soaps are prepared in our laboratory and stocked for two years; the former does not entirely differ during its storage while the latter changed its color to brown in the same way as soaps which are sold commercially and also grow much "sweat." The hydrolysis degrees of their $\frac{N}{50}$ solutions are as follows:

TABLE VII.

Names of Soaps.	Mean M. wt. of fatty acids.	Hydrolysis degree		Difference.
		by Tit.-method.	by Tol.-m.	
Na-soap of Soya Bean Oil	292.1	2.02	23.25	+21.03
do of Tallow	284.6	57.99	40.00	-17.99

In the hydrolysis, the Soya Bean Oil soap plays just the same part as those of soaps F, H and I in Table V. After the addition of sulphuric acid to the soap solution the free fatty acids were separated from these soaps and were treated with petroleum-ether, in which the oxidised acids are insoluble.

It was found that 48.5% of the soya bean fatty acids were oxidised, whilst only about 3% of the tallow acids had been oxidised. For this reason, I compared the influences of oxidised and non-oxidised fatty acids upon the hydrolysis of soaps, adding them to the solution of sodium soaps of stearic acid separately and investigated the hydrolysis of each solution. The results are given in Table VIII. The amount of added acid was 20% of the acid in the soap solution $\left(\frac{N}{50}\right)$.

TABLE VIII.

Name of Soap.	Fatty acid added.	Hydrolysis by Tit. method.
Na-soap of stearic acid	0	64.25%
" " " "	non-oxidised fatty acid.	50.25
" " " "	oxidised fatty acid.	37.00

The effect of the oxidised fatty acid on the hydrolysis of soap is much greater than that of the nonoxidised fatty acid. If a soap contains oxidised fatty acid, the hydrolysis of that soap as measured by means of the Titration method, will not be large because the development of a fatty acid as the result of hydrolysis will tend to prevent further hydrolysis. In the Toluene-method the fatty acid is removed into the toluene layer and therefore it cannot prevent the further hydrolysis of that soap. This is the reason why the Toluene-method cannot be applied to the soap when it has some oxidised fatty acid as its component.

With reference to this I am thankful to Mr. Ogawa of the Imperial Experimental Station of Silk Industry for assisting me to complete my experiment.

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